

SYSTEMS AND METHODS FOR GENERATING POLYSULFIDES

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority from U.S. Provisional Patent Application No. 60/420,144, entitled "Surface Coated Products Used in Polysulfide Generation and Methods for Their Production" and filed October 22, 2002. The disclosure of the above-mentioned provisional application is incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

In the conventional kraft cooking process, two chemicals, namely sodium hydroxide (NaOH) and sodium sulfide (Na₂S), are used to delignify wood chips. During the course of the reaction, part of the undesired fraction of wood, lignin, is solubilized and removed. However, cellulose and hemicelluloses, which are desirable polysaccharide components of the wood, are also attacked. Hence, one of the goals sought during cooking is to protect this fraction in order to achieve a better process yield.

The weight contribution of these components varies with each wood species, but it is usually around 70%. In an industrial process, however, the amount retained is often around 45-50%. Typically, 80% of the lignin, 50% of the hemicelluloses and 10% of the cellulose are removed. The hemicelluloses are easily attacked because they are low molecular weight sugars that are more accessible than the crystalline cellulose. They are removed by what is called "alkaline peeling," which occurs at the reducing end group of the polymeric chain.

It is well known in the art that sodium polysulfide (Na₂S_n wherein $n \geq 2$), herein referred to as "polysulfide," can be introduced in a digester to increase the carbohydrate yield in the kraft cooking process. This prevents the degradation of the polysaccharides and increases the lignin yield. Haegglund first discussed this concept in 1946 (Svensk Papperstidn. 49(9): 191, 1946). Polysulfide can be generated by different means. In one approach, polysulfide is formed by adding elemental sulfur to white liquor. White liquor, as it is commonly known in the art, is the liquid that comes in contact with the pulping materials, generally wood chips, during the cooking process. Adding elemental sulfur to the white liquor, however, may lead to sulfur imbalances in the chemical recovery cycle,

leading to sulfur build-up that will eventually be released to the atmosphere as sulfur gas emission. For this reason, this approach has very limited industrial interest.

A second approach involves chemically oxidizing the sodium sulfide present in the white liquor to polysulfide. The resulting liquor containing polysulfide is known in the art as orange liquor.

Several variations of this oxidation method producing polysulfide have been published:

1) In U.S. patent No. 3,470,061 Barker discloses a method using inorganic manganese oxides as the oxidant. The oxidation occurs in an external recycle loop after the catalyst has been separated and dried. One of several drawbacks to this process, however, is that the presence of sodium sulfide in the white liquor prior to the clarifier can result in problems with the lime mud.

2) In U.S. patent No. 3,860,479, Barker et al. discloses a method in which manganese dioxide is an oxidation catalyst comprising a slurry or packing in a tower. The catalyst contacts an oxygen source that helps it maintain its oxidative state. This process shares many of the drawbacks of US patent No. 3,470,061.

3) In U.S. patent No. 4,024,229 Smith discloses a method to produce polysulfide through chemical oxidation, using particulate carbon coated with PTFE as the catalyst. The method is said to reduce the production of sodium thiosulfate ($\text{Na}_2\text{S}_n\text{O}_3$), an undesirable compound. One drawback to this process is that the catalyst bed has to be regenerated due to particles of calcium carbonate deactivating the catalyst.

4) In U.S. patent No. 4,855,123 Suzuki et al. discloses a method similar to that of US Patent No. 4,024,229 but uses activated carbon for the catalyst. This invention has the same drawbacks as US patent No. 4,024,229.

5) In U.S. patent No. 5,624,545 Landfors et al. discloses a method to produce polysulfide through electrolysis of the white liquor. This method involves high capital and energy costs.

6) In U.S. patent No. 5,082,526 Dorris discloses a method to produce polysulfide in the presence of lime mud. One disadvantage of this method is that it requires a long oxidation time, leading to a lower selectivity because of over-oxidation and thermal degradation of polysulfide. Another disadvantage is that the white liquor must be sent with its lime mud contents to the oxidation process, which increases oxygen usage and equipment cost.

As described, there are several processes for producing polysulfide from white liquor to increase the cellulose and hemicelluloses yield in kraft cooking. However, these processes are often either complicated or not cost-effective.

OBJECTS AND SUMMARY OF THE INVENTION

5 Therefore, in light of the above, and for other reasons that become apparent when the invention is described, an object of the present invention is to provide a simple, efficient, long-lasting, and cost-effective system and process to oxidize sodium sulfide to become sodium polysulfide in kraft cooking liquors without the drawbacks of prior art methods.

10 Another object of the present invention is to provide a system and process that increases the production of polysulfide and minimizes the amount of sodium thiosulphate produced.

A further object of the present invention is to provide a system and process that is flexible in its application, because it will not be limited by the presence of lime mud in the white liquor and can be used prior to and/or after clarification.

15 The aforesaid objects are achieved individually and in combination, and it is not intended that the present invention be construed as requiring two or greater of the objects to be combined unless expressly required by the claims attached hereto.

20 In accordance with one embodiment of the present invention, a process for generating polysulfide in a pulping liquor includes the steps of: providing a pulping liquor containing sodium sulfide, providing at least one oxidation promoter element including an oxidation promoter adhered by a coating material to a substrate, and contacting the oxidation promoter element with the pulping liquor so as to generate polysulfide in the pulping liquor.

25 In accordance with another embodiment of the present invention, a system includes at least one vessel for containing the pulping liquor, including an inlet to facilitate the flow of pulping liquor into the vessel, and an outlet to facilitate the flow of pulping liquor from the vessel. The system further includes at least one oxidation promoter element including an oxidation promoter at least partially embedded in a coating material that at least partially coats a substrate, where the oxidation promoter promotes the oxidation of the sodium sulfide to generate polysulfide. The oxidation promoter element is positioned within the vessel to contact the pulping liquor.

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One or more oxidation promoter elements may be disposed in one or more vessels, with the oxidation promoter elements further being affixed or movable (e.g., rotatable) within the vessels. The vessels may further be configured to receive at least one oxidizing agent to increase the oxidative state of the oxidation promoter disposed in each vessel.

In accordance with a further embodiment of the present invention, a system and corresponding methods for generating polysulfide in accordance with the present invention include a polysulfide generation zone that receives pulping liquor including sodium sulfide to facilitate the generation of polysulfide, a recovery zone that receives at least one oxidizing agent, and at least one oxidation promoter element that is movable between the polysulfide generation zone and the recovery zone. The oxidation promoter element preferably includes a substrate with a coating material disposed thereon, where the coating material includes an oxidation promoter that promotes oxidation of the sodium sulfide in the pulping liquor to generate polysulfide. Polysulfide is generated from sodium sulfide within the pulping liquor when the oxidation promoter element is situated within the polysulfide generation zone, and the oxidative state of the oxidation promoter is increased when the oxidation promoter is situated within the recovery zone and in contact with the at least one oxidizing agent

The polysulfide generation and recovery zones can each include one or more vessels, and the oxidation promoter element can include a plurality of elements, where each oxidation promoter element is movable between a vessel for the polysulfide generation zone and a corresponding vessel for the recovery zone.

The above and still further objects, features and advantages of the present invention will become apparent upon consideration of the following detailed description of specific embodiments thereof, particularly when taken in conjunction with the accompanying drawings wherein like reference numerals in the various figures are utilized to designate like components.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic of the polysulfide formation process using the oxidation promotion element, according to the invention.

FIG. 2 is a side view in elevation of the oxidation promoter element in a vessel according to the invention.

FIG. 3 is a cross-sectional view of a first embodiment of the oxidation promoter element.

FIG. 4 is a cross-sectional view of a second embodiment of the oxidation promoter element according to the invention.

5 FIG. 5 is a perspective view of a third embodiment of the oxidation promoter element according to the invention.

FIG. 6 is a cross-sectional view of FIG. 5.

FIG. 7 is a view in perspective of an embodiment FIG. 5 in a vessel.

FIG. 8 is a view in perspective of another embodiment of FIG. 5 in a vessel.

10 FIG. 9 is a side view in elevation of an embodiment of the substrate.

FIG. 10 is a side view in elevation of an embodiment of the oxidation promoter element.

FIG. 11 is a perspective view of a sleeve configuration incorporating a number of elements of FIG. 10.

15 FIG. 12 is a side view in elevation of the oxidation promoter element of FIG. 9 fixed to a vessel according to the invention.

FIG. 13 is a side view in elevation of the oxidation promoter element fixed to a vessel.

20 FIG. 14 is a side view in elevation of the oxidation promoter element in a washer configuration.

FIG. 15 is a side view in elevation of a system including a vessel with inlet and outlet ports and the oxidation promoter element.

25 FIG. 16 is a side view in elevation and partial section of a system including a vessel containing an oxidation promoter element in the form of a sleeve, a hollow shaft, and an impeller.

FIG. 17 is a side view in elevation and partial section of the system of FIG. 16, further including an oxygen-containing gas supply conduit.

FIG. 18 is a side view in elevation and partial section of the system of claim 17, further including a caustic agent (sodium hydroxide) supply.

30 FIG. 19 is a side view in elevation and partial section of a dual vessel configuration of vessels with inlet and outlet ports, a Hollow Shaft, an impeller, and the oxidation promoter element.

FIG. 20A is a cross-sectional view of a dual-vessel system including a recovery zone and a polysulfide generation zone.

FIG. 20B is a top plan view of the system of FIG. 20A.

FIG. 21 is a cross-sectional view of a system including a plurality of polysulfide generation zones separated by a recovery zone.

FIG. 22 is a top plan view of the system of FIG. 21.

FIG. 23 is a partially exploded view in perspective of a system including a polysulfide generation zone and a recovery zone and rotatable discs.

FIG. 24 is a cross-sectional view of the system of FIG. 23.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As seen in **FIG. 1**, the method of the invention includes an oxidation promoter element **1** contacting sodium sulfide **2** contained within a pulping liquor, which is oxidized to create polysulfide **3**. The oxidation promoter element **1** includes a substrate, a coating material, and an oxidation promoter. The oxidation promoter element **1** may oxidize the sodium sulfide **2** itself, or it may catalyze oxidation of the sodium sulfide **2** by an oxidizing agent **4**. If an oxidizing agent serves as the oxidation promoter element **1**, its oxidation state may decrease during the sodium sulfide reaction, but the oxidation state is recovered by oxidizing the oxidation promoter element **1** itself back to the beginning or initial oxidation state.

As shown in **FIG. 2**, the system of the invention includes the oxidation promoter element of **FIG. 1** contained within a vessel **5** containing pulping liquor **6** where it is oxidized to generate polysulfide. Vessel **5** includes an inlet **7** and an outlet **8**, through which the pulping liquor flows into and out of the vessel **5**, at which time it includes polysulfide generated by oxidation of sodium sulfide. The vessel is a non-limiting configuration that may further include a process line, a tank, or a column.

While practice of the invention may be for oxidizing sodium sulfide in various solutions, the solution discussed herein is pulping liquor. Preferably, the pulping liquor to be oxidized is what is commonly known in the art as "white liquor," although other pulping liquors may be used, such as "green liquor" or "black liquor". After oxidation of the sodium sulfide is achieved, the liquor contains polysulfide, and is commonly known in the art as "orange liquor." The phrases "white liquor", "green liquor", "black liquor", and "orange liquor" are well known in the kraft pulping art as defined, for example, by

Grace, T. M. and Malcolm, E. W., "Pulp and Paper Manufacture", Volume 5, 3rd Edition, 1989, and Dorris, G. M., "Oxidation of White Liquor in the Presence of Lime Mud", Pulp and Paper Canada, 95:10 (1994), the disclosures of which are incorporated herein by reference in their entireties. The white liquor is generally clarified in a clarifying tank prior to oxidation; however, unclarified liquor may also be used. One advantage to the invention is that it may perform to generate polysulfide from sodium sulfide in unclarified liquor. Normally the presence of lime mud in the unclarified liquor would interfere with sodium sulfide contacting an oxidizing agent, but use of the invention allows enough contact points between the oxidation promoter element and the sodium sulfide for sodium sulfide oxidation to occur and generate polysulfide.

Other advantages to the invention include how it limits possible negative outcomes to the sodium sulfide oxidation process. If sodium sulfide and a newly formed polysulfide remain in contact with an oxidizing agent for an extended period of time, the selectivity of polysulfide formed may decrease. Selectivity is defined by $((\text{polysulfide formed}) / (\text{converted sulfide})) / 100$. This differs from yield, which is defined by $((\text{polysulfide formed}) / (\text{initial sulfide})) / 100$. High selectivity indicates that a large content of the sodium sulfide was converted to polysulfide, while high yield only indicates that a large content of sodium sulfide underwent conversion but did not necessarily form polysulfide. Low selectivity may result if sodium sulfide is exposed to an oxidizing agent for too long, causing the sodium sulfide to be converted into undesirable products that contribute to the process deadload. One of these undesirable products is sodium thiosulfate ($\text{Na}_2\text{S}_n\text{O}_3$ where $n \geq 2$), herein referred to as "thiosulfate," which not only leads to process deadload but also is corrosive.

The present invention helps to minimize the possible occurrence of these outcomes. The white liquor contacts the oxidation promoter element for a length of time sufficient to allow the sodium sulfide to form polysulfide. The oxidation promoter element causes polysulfide to form relatively quickly. As a result, it limits the number of side reactions that could occur with the sodium sulfide, such as thiosulfate formation. The contact time between the oxidation promoter element and the sodium sulfide is short enough to prevent a substantial amount of thiosulfate from forming, and selectivity is increased. Furthermore, the invention's efficiency in oxidizing sodium sulfide leads to forming a high ratio of active to inactive polysulfide.

As best shown in **FIG. 3**, the oxidation promoter element **1** is made of a substrate **9**, a coating material **10**, and an oxidation promoter **11**. The substrate **9** serves as a solid support for the oxidation promoter element **1** and may be comprised of any one or more of a variety of materials, including metals, thermosetting plastics, nylons, clays, bricks, ceramics, and the like. Preferably, the substrate is stainless steel.

The coating material **10** adheres the oxidation promoter **11** to the substrate **9** and at least partially covers the substrate **9**. The coating material **10** may be comprised of any one or more of a variety of materials, including organic polymers, inorganic polymers, metals, clays, bricks, ceramics, thermosetting plastics, resin types, and the like. Preferably, coating material **10** is an organic polymer. A specific example of an epoxy resin for use as a coating material is a formulation sold under the trade name Impreglon™ (e.g., Impreglon™ 817), available from Impreglon, Inc., Houston TX.

The oxidation promoter **11** promotes the oxidation of sodium sulfide in the pulping liquor. The oxidation promoter **11** is at least partially embedded in the coating material **10** such that a portion of the oxidation promoter **11** is available to contact the sodium sulfide, while another portion interfaces with the coating material **10**. The oxidation promoter **11** may be comprised of transition metal oxides, transition metals, or adsorbents. As a transition metal oxide, the oxidation promoter **11** serves as an oxidant to oxidize sodium sulfide. A preferred transition metal oxide is manganese dioxide. In addition, transition metals or adsorbents catalyze the oxidation of sodium sulfide by an oxidant. Suitable transition metals include platinum, nickel, cobalt, and the like. Suitable adsorbents include carbon, silica, aluminum, zeolites, and the like. Whether the sodium sulfide is oxidized directly by oxidation promoter element **1**, or the oxidation promoter element catalyzes this oxidation, both serve to promote oxidation of the sodium sulfide.

To at least partially embed the oxidation promoter **11** within the coating material **10**, the coating material **10** and the oxidation promoter **11** may be subjected to different treatments. For example, the coating material **10** can be formed via a spray, followed by pressing the oxidation promoter **11** on the coating material **10**. The coating material **10** and oxidation promoter **11** are then baked together. Alternatively, the coating material **10** may not be baked and the oxidation promoter **11** may be pressed into the coating material **11**. The coating material **10** may also be made of ceramic pre-forms with the oxidation promoter **11** blasted on top of the coating material **10**, followed by backing the pre-forms.

As seen in **FIG. 4**, the oxidation promoter **11** and coating material **10** may be configured as a matrix composition. To illustrate, the oxidation promoter **11** may be embedded in a matrix comprised of the coating material **10** that coats the substrate **9**. A portion of at least some of the oxidation promoter **11** is left uncovered by the coating material **10** so that it may contact the sodium sulfide. In order to prepare the matrix such that at least some of the surface of the oxidation promoter **11** is exposed, the outer surface of the matrix may be mechanically abraded, sandblasted, or selectively dissolved to uncover the oxidation promoter **11**.

Aside from the previously discussed relationship between the substrate **9**, the coating material **10**, and the oxidation promoter **11**, the oxidation promoter element **1** may be structured in various configurations that apply to open or closed systems. For example, the oxidation promoter element **1** may comprise a screen placed perpendicularly to the flow of sodium sulfide in a process line such that the sodium sulfide flows through the screen. Additionally, as shown in **FIG. 5**, the oxidation promoter element may possess what is herein called a “bead” configuration **12**. Illustrated in the embodiment of **FIG. 6**, the substrate **9** is formed into a spherical shape, forming a bead. Bead **12** is then covered with the coating material **10** having the oxidation promoter **11** partially embedded therein. The bead **12** may be any shape or size that allows the sodium sulfide to form polysulfide. For example, the bead may be shaped like a sphere, an ellipsoid, a flattened disc, a fiber, or may possess an irregular shape. Preferably, the bead has a major dimension of less than about 40 cm. More preferably, the major dimension of the bead is less than about 20 cm. Most preferably, the major dimension of the bead is less than about 2 cm.

As shown in **FIG. 7**, a number of beads **12** could be adhered to a solid support **14** (here, a series of rods) that is fixed with vessel supports (a rod **22** and a base **23**) to the bottom of a vessel **21**. Also, as in **FIG. 8**, the beads **12** may float freely in vessel **21** so that the liquid containing sodium sulfide **18** may flow around the suspended beads. The beads may also occupy a packed column, similar to a configuration described in U.S. patent No. 3,860,479 to Barker et al., which is incorporated herein by reference in its entirety.

Another configuration of the oxidation promoter element is herein called a “sleeve” configuration. It is prepared by first shaping the substrate **9** into a rectangular coupon **19**, as shown in **FIG. 9**. As illustrated in **FIG. 10**, each coupon **19** is then

covered with the coating material **10** having the oxidation promoter **11** partially embedded therein. As shown in **FIG. 11**, a series of these coupons **19** are placed in parallel and circumferentially disposed about an axis of a ring **20**, securing them to one another, and forming a sleeve **24**. The coupons **19** are spaced apart on the ring **20** so that
5 the liquid containing sodium sulfide may flow between the coupons **19**. For example, the rings may be spaced about 0.25 cm apart. The coupons, while rectangular, may possess other shapes, and may be of any size. The ring center (and thus sleeve **24**) is open such that the sodium sulfide is allowed to flow therein and thereout, maximizing the surface contact of the sodium sulfide with oxidation promoter element (i.e. the sleeve).

10 The oxidation promoter element may be stationary or moving within a vessel. To illustrate a stationary structure, as shown in **FIG. 12**, the oxidation promoter element **1** is placed in a vessel **21** such that it rests in a stationary position on the bottom of the vessel **21** in any suitable manner. As shown in **FIG. 13**, the element (here, a sleeve) may be fixed to a vessel by attaching one end of a rod **22** to the ring **20** of sleeve **24**, while fixing
15 the other end of the rod **22** to the vessel **21** using a support base **23**. One of ordinary skill in the art will understand that many other suitable structures for the supports are suitable for practice of the invention.

An embodiment in which the oxidation promoter element moves in relation to a vessel **21** is shown in **FIG. 14**. Sleeve **24** is placed horizontally within a vessel **21**. The
20 sleeve **24** has a shaft **25** in its center connected by several rods **26** to the shaft ring **20**. The shaft **25** extends beyond the vessel **21** through a vessel aperture **27** and is connected to a rotor **28**. The rotor **28**, driven by a motor **29**, turns the shaft **25**, causing the sleeve **24** to rotate within the vessel **21**. This is herein referred to as the “washer” configuration.

The oxidation promoter element may be used to produce polysulfide in a batch
25 process, a continuous process and/or a combination thereof. A batch process may include a single vessel or multiple vessels in which polysulfide is created in the white liquor. **FIG. 15** illustrates a batch process with a single vessel **21**, in which white liquor enters the vessel through an inlet **30** and contacts the oxidation promoter element. One skilled in the art will recognize that the manufacturing of polysulfide and selection of an amount
30 of oxidation promoter to use per amount of sodium sulfide to be converted to polysulfide is a function of well known operating parameters, such as the reaction kinetics of converting sodium sulfide to polysulfide and the amount of oxidation promoter required per amount of sodium sulfide provided in the liquor.

In polysulfide mode, the white liquor enters the vessel until a specific parameter to stop the white liquor flow is fulfilled. These parameters may include vessel level (determined by a level detector on the inner wall of the vessel) and/or time of flow (determined by a timer in communication with a white liquor flow control valve). After the required retention time for the white liquor to remain in the vessel expires, the white liquor containing polysulfide, now called orange liquor, exits the vessel through an outlet 31. To illustrate a continuous process with a single reactor, a vessel may be constructed with a similar configuration as the batch process in FIG. 15, except that the white liquor entry into and exit out of the vessel 21 is generally ongoing. For both processes, the white liquor flow into and out of the vessel 21 is controlled to allow sufficient time for the sodium sulfide to form polysulfide without proceeding to thiosulfate formation.

As sodium sulfide is oxidized to form polysulfide, it is advantageous to create as many contact points as possible between the sodium sulfide and the oxidation promoter element to make polysulfide formation more efficient. One way to achieve this is to agitate the sodium sulfide with a rotating device. As seen in FIG. 16, the sleeve 24 can be placed in a stationary position in a vessel 21 by fixing the sleeve ring 20 to a rod 22 that, in turn, is attached to the bottom of the vessel 21 using a support base 23. A hollow shaft ("shaft") 32 is provided with a three-blade impeller 33 positioned at its end. Shaft 32 is a hollow, rod-shaped device that allows material to enter through a shaft inlet 34, flow through the shaft 32, and exit through a shaft outlet 35 at the shaft's end. The hollow shaft 32 is more fully described in U.S. Patent 6,517,729, which is incorporated herein by reference in its entirety. In the embodiment of FIG. 16, the shaft 32 and impeller 33 are inserted through the central portion of the sleeve 24; however, they may be located at any point in the vessel 21. When the white liquor enters the vessel 21 through an inlet 30, the impeller 33 agitates the liquor such that it travels around the vessel 21, increasing its contact with sleeve 24. Any material introduced through shaft inlet 34 is also mixed into the white liquor as the material exits through shaft outlet 35. Once reacted, the solution exits the vessel via outlet 31. Mixing may also be achieved with the washer configuration shown in FIG. 14 as the sleeve rotates within the vessel.

In addition to mixing, the efficiency of forming polysulfide in the white liquor is increased when the oxidation promoter is a transition metal oxide. The transition metal oxide acts as an oxidizing agent that oxidizes sodium sulfide to create polysulfide, and it may do this in less than about 20 minutes (e.g., about 10-20 minutes). More specifically,

with manganese dioxide as the oxidation promoter, it only takes about 1 minute for 1 gram of manganese dioxide per liter of white liquor to produce 0.77 grams of polysulfide per liter of white liquor. Because the transition metal oxide is reduced when it oxidizes the sodium sulfide, its oxidative state needs to be restored so that more sodium sulfide may be oxidized. This is achieved by exposing the transition metal oxide to an oxidizing agent. Suitable oxidizing agents include O₂, O₃, oxygen-enriched air, peroxides, and the like. One preferred oxidizing agent is oxygen-enriched air. For example, oxygen-enriched air may be obtained by premixing air with oxygen at selected proportions to achieve a desired result, namely, restoration of the transition metal oxide to a selected oxidative state. The source of oxygen supply can be obtained, e.g., from various locations within the pulp and/or paper mills. This obtained oxygen supply can also be enriched with a suitable supply of fresh oxygen, as desired.

Controlling the temperature of the reaction liquids can also increase efficiency. Since the production of polysulfides is dependent on temperature and the oxidation reaction of white liquor is exothermic, it is important to control the temperature to minimize oxidation of Na₂S to sodium thiosulphate (Na₂S₂O₃). For this reason, the system vessel may be equipped with heating jackets and cooling coils to maintain the desired temperature. The temperature of the reaction liquids is preferably kept in the range of from about 50°C to about 120°C, and more preferably from about 75°C to about 85°C. The manufacturing of polysulfide, selection of an amount of oxidation promoter and/or oxidizing agent to use per amount of sodium sulfide to be converted to polysulfide is described in detail in copending U.S. Patent Application No. 09/784,076, filed on February 16, 2001, which is incorporated herein by reference in its entirety.

There are several ways to expose the transition metal oxide to an oxidizing agent. For example, as in **FIG. 17**, a system includes a vessel **21** with a stationary sleeve **24** positioned therein. A hollow shaft **32** with impeller **33** is further positioned within the sleeve. When the system performs as a continuous process to generate polysulfide, an oxygen-containing gas such as oxygen-enriched air may be added to the vessel. While 70% oxygen content is preferred in the oxygen-containing gas, oxygen contents greater or less than 70% may be used. Pure oxygen may also be used, but oxygen-enriched air is preferred in this configuration in order to avoid over-oxidation of sodium sulfide, which may lead to substantial thiosulfate production. A sodium sulfide containing liquid (here, white liquor) **37** enters the vessel through inlet **30**. Once the vessel is filled, oxygen-

containing gas from a conduit or carrier line 80 enters the vessel 21 through an inlet 36 such that it is mixed into the white liquor 37. The oxygen-containing gas flows up through the liquor and occupies headspace 38 in the vessel above the white liquor's surface. Alternatively, the oxygen-containing gas may be introduced directly into the headspace 38. The oxygen-containing gas then enters the shaft inlet 34 and flows through the shaft 32, exiting through the shaft outlet 35 near the impeller 33. When the oxygen-containing gas exits the shaft 32, the rotating impeller 33 mixes the gas into liquor 37 and distributes it around the sleeve. In this manner, a convection current is created in which oxygen-containing gas is dispersed to the middle and periphery of the vessel 21 and then the unreacted or remaining gas rises up to the surface of liquor 37 into headspace 38. It then re-enters the hollow shaft 32 through the shaft inlet 34. The reacted liquor then exits through an outlet 31. This distribution improves the availability of the oxygen-containing gas to oxidize the sodium sulfide and also to help the transition metal oxide recover its oxidative state. Thus, in the continuous process, polysulfide and recovery modes occur simultaneously.

Recovery of the oxidation promoter's oxidative state may also be performed in a batch process. The system embodiment of FIG. 18 includes a vessel 21 with a stationary sleeve 24 positioned therein. In this batch process, the white liquor enters the vessel through an inlet 30, and remains in the vessel for a time period sufficient to create a desired amount of polysulfide. The reacted, orange liquor is then discharged from the vessel through an outlet 31. This is referred to as the "polysulfide mode". After the orange liquor exits the vessel 21, a caustic agent such as sodium hydroxide is added to the vessel through an inlet 39. An oxygen-containing gas enters vessel 21 from a conduit 80 through an inlet 36, such that it is mixed into and flows up through the sodium hydroxide to occupy the headspace 38 in the vessel above the sodium hydroxide's surface. The oxygen gas then enters the shaft inlet 34, flows through the shaft 32, and exits through shaft outlet 35 near the impeller 33. Preferably, pure oxygen or very highly oxygen-enriched air is used because the process is not in polysulfide mode when the oxygen-containing gas is added, so there is no concern about forming thiosulfate. The sodium hydroxide and the oxygen-containing gas react with the transition metal oxide so that it recovers its oxidative state. This is referred to as the "recovery mode". Those skilled in the art will understand that when adsorbents as the oxidation promoter, they need not be oxidized. The retention time of the sodium hydroxide and oxygen gas in the vessel

should be sufficient for the oxidative state of the transition metal oxide to be recovered, which may be as little as about 3-5 minutes.

Following this recovery, the sodium hydroxide, plus other remaining vessel contents, are discharged from the vessel **21** through an outlet **40**. Although **FIG. 18** shows different inlets **30**, **39** for the white liquor and the sodium hydroxide flows, respectively, both flows may enter the vessel through the same inlet, so long as the two flows are not mixed. This can be achieved, e.g., by using flow-control and check valves. Similarly, both the polysulfide and sodium hydroxide outlet flows may exit the vessel **21** through a same outlet. The discharge from the recovery process may be sent to a sodium hydroxide holding tank **41**. To reduce costs, the contents of the sodium hydroxide holding tank **41** may be re-used several times for recovery mode. After the sodium hydroxide and other contents have exited the vessel **21**, white liquor is once again added to the vessel through inlet **30** to repeat the batch process in polysulfide mode.

Polysulfide generation and recovery of the oxidation promoter may be carried out separately, yet simultaneously, by utilizing at least two vessels. In this embodiment, while one vessel is in polysulfide mode, the other vessel or vessels is/are in recovery mode. Each of the vessels need not have identical configurations or other parameters. When a particular vessel has completed its respective mode, the remaining contents of that mode are discharged, as described in the batch process above. This discharge may or may not occur at the same time and is generally dependent on the process design. After the contents in each vessel have been at least partly discharged, each vessel is filled with the necessary contents for the other mode, which then proceeds in each vessel. Thus, if a vessel completes polysulfide mode, at least part of, if not all of, the liquor is discharged and the vessel is filled with sodium hydroxide and an oxygen-containing gas to carry out recovery mode.

The embodiment of **FIG. 19** illustrates a multi-vessel system. In this system, vessel 1 **21a** and vessel 2 **21b** are part of a dual-vessel configuration, in which each vessel contains a hollow shaft **32a**, **32b** equipped with an impeller **33a**, **33b**. The shaft is positioned with a sleeve **24a**, **24b**. Vessel 1 **21a** is filled with white liquor through an inlet **30a** and then the polysulfide mode is performed. During this time, vessel 2 **21b** is filled with sodium hydroxide through a second inlet **39b**. Oxygen-containing gas enters vessel 2 **21b** from a carrier line **80b** through a gas inlet **36b**, such that it is mixed into and flows up through the sodium hydroxide to occupy the headspace **38** in the vessel above

the sodium hydroxide's surface. The oxygen-containing gas then enters the shaft inlet **34b**, flows through the shaft **32b**, and exits through shaft outlet **35b** near the impeller **33b**. Thus, vessel 2 **21b** performs and completes the recovery mode.

After each mode is completed, the polysulfide products are discharged through the outlet **31a** of vessel 1 and the recovery products are discharged through outlet **40b** of vessel 2. Then, vessel 1 **21a** can be filled with sodium hydroxide through an inlet **39a**, and oxygen-containing gas can enter from a carrier line **80a** through a gas inlet **36a** so that recovery mode will proceed in vessel 1 **21a**, similar to how recovery mode proceeded in vessel 2 **21b**. During this time, vessel 2 **21b** is filled with white liquor through an inlet **30b** so that polysulfide mode will proceed in vessel 2 **21b**, similar to polysulfide mode in vessel 1 **21a**. To reduce cost, the carrier lines **80a**, **80b** may be connected to a single oxygen-containing gas source **44**. In this system, like the single-vessel continuous process, polysulfide mode is not interrupted for the purpose of recovering the oxidative state of the oxidation promoter. Like the single-vessel batch process, however, the oxidation promoter is always in its most reactive state when white liquor enters the vessel **21a** or **21b** to generate polysulfide. As described above, instead of using separate inlet and outlets for the white liquor and sodium hydroxide, a single inlet and/or outlet may be used.

Another system configuration establishes a "recovery zone" and a "polysulfide generation" zone, wherein the oxidation promoter element is capable of moving between the two zones. The term "polysulfide generation zone" refers to any vessel or portion of the system that generates polysulfide from sodium sulfide in the pulping liquor, whereas the term "recovery zone" refers to any vessel or portion of the system that facilitates the recovery of the oxidation promoter element to its initial oxidative state (i.e., its oxidative state prior to promoting generation of polysulfide).

One embodiment of the configuration is shown in **FIGS. 20A** and **20B**. In this embodiment, a tank **82** is partitioned into two separate vessels. Vessel 1 **21a** (the polysulfide generation zone) includes an inlet **30** and an outlet **31**. Vessel 2 **21b** (the recovery zone) includes a carrier line **80**, an inlet **39** and an outlet **40**. A supporting member **48** is positioned above tank **82**. Flag members **47a**, **47b** are attached to support member **48**. Each flag includes an arm **46a**, **46b** connected to the support member at one end and to a coupon **19a**, **19b** at the other. The coupons are similar to those described above. The size of the coupons is not particularly limited, and may be of any shape. The

arms, moreover, are capable of substantial rotation (e.g., about 270°) about support member **48** such that the coupons can be rotated from vessel 1 **21a** to vessel 2 **21b**. In use, the white liquor enters vessel 1 **21a** through inlet **30** and sodium hydroxide enters vessel 2 **21b** through inlet **39**. Oxygen-containing gas from conduit **80** enters vessel 2 **21b** through a gas inlet **36**, such that it is mixed into and flows up through the sodium hydroxide.

The flags are suitably positioned such that coupon **19a** of flag **47a** is contained in vessel 1 **21a** while coupon **19b** of flag **47b** is contained in vessel 2 **21b**. This enables the flag contained in vessel 1 to be immersed in the white liquor, and the flag contained in vessel 2 to be immersed in the sodium hydroxide solution. The flags remain immersed for the desired time period (i.e., the time necessary to produce polysulfide). Preferably, vessel 1 **21a** is sparged with an inert gas, such as nitrogen, to decrease or limit entry of oxygen into vessel 1 **21a**.

When the white liquor has reacted to the desired degree, it (now in the form of orange liquor) may be removed from vessel 1 **21a** via outlet **31**. The sodium hydroxide, moreover, is discharged using outlet **40**. Alternatively, as described above, instead of using separate inlet and outlets for the white liquor and sodium hydroxide, a single inlet and/or outlet may be used. Moreover, to reduce operating costs, the sodium hydroxide may be used for several recovery processes before being discharged. Thus, recovery vessel 2 **21b** can be a batch tank, while the liquor flows continuously through vessel 1 **21a**. However, it is noted that each vessel may be batch, semi-batch or continuous.

While draining, the position of the flags can be reversed. That is, the flags can be repositioned such that coupon **19a** of flag **47a** is now contained in vessel 2 **21b** (immersed in the sodium hydroxide) and coupon **19b** of flag **47b** is contained in vessel 1 **21a** (immersed in the white liquor). White liquor again fills vessel 1 **21a**, and the process can be repeated. Thus, vessel 1 **21a** generates polysulfide and vessel 2 **21b** performs and completes recovery of the oxidation promoter. Though the current embodiment discloses two flags, any number of flags may be utilized (e.g., three or more). The flags may be of any shape or size, and may be positioned in any desired configuration to enable their selective immersion in either the recovery zone or the polysulfide generation zone. Additionally, it is noted that, depending upon a particular processing scenario, the flags may be rotated one or more times during a reaction cycle.

FIGS. 21 & 22 disclose a configuration including a plurality of polysulfide generation zones separated by a recovery zone. Referring to **FIG. 22**, a tank **82** is partitioned into three vessels. Specifically, a recovery zone vessel **92** is positioned between two polysulfide zone vessels **90, 94**. A first support member **54** is positioned directly over a partition wall separating the first polysulfide zone vessel **90** and the recovery zone vessel **92**. The first support member is suitably positioned to permit the rotation of flags into both the first polysulfide zone vessel **90** and the recovery zone vessel **92**. Similarly, a second support member **56** is suitably positioned directly over the partition wall separating the recovery zone vessel **92** and the second polysulfide zone vessel **94** to permit the rotation of flags into both the recovery zone vessel **92** and the second polysulfide zone vessel **94**. The polysulfide zone vessels **90, 94** include inlets **30a, 30b** and outlets **31a, 31b** (though a single port may serve as both an inlet and an outlet). The recovery zone vessel **92** includes a fluid inlet **39**, a fluid outlet **40**, and a gas inlet **36** through which oxygen-containing gas delivered via conduit **80** enters.

The number and position of flags are not limited. In the current embodiment, at least one flag is positioned within the recovery zone vessel and at least one flag is positioned within one or both the first and second polysulfide zone vessels. Referring particularly to **FIGS. 21 and 22**, flags **47a-d** are rotatably attached to support member **54** in alternating positions. Specifically, flags **47a, 47c** are positioned such that coupons **19a, 19c** are contained in the first polysulfide zone vessel **90** (to enable immersion in the white liquor), and flags **47b, 47d** are positioned such that coupons **19b, 19d** are contained in recovery vessel (to enable immersion into the sodium hydroxide). Similarly, flags **47e-h** are rotatably attached to support member **56** in alternating positions, with flags **47e, 47g** positioned such that coupons **19e, 19g** are contained in the second polysulfide zone vessel **94** (to enable immersion into the white liquor), and flags **47f, 47h** are positioned such that coupons **19f, 19h** are contained in the recovery zone vessel **92** (to enable immersion in the sodium hydroxide).

In use, the polysulfide generation zone vessels **90, 94** are filled with white liquor via inlets **30a, 30b**. The recovery zone vessel **92**, moreover, is filled with a caustic agent such as sodium hydroxide, and an oxygen-containing gas flows through the sodium hydroxide, entering via gas inlet **36**. As explained above, coupons **19a, 19c, 19e, 19g** are positioned within the polysulfide generation zone vessels **90, 94** and coupons **19b, 19d, 19f, 19h** are positioned within the recovery zone vessel. The coupons in the polysulfide

zone vessel contact the white liquor for a time suitable to generate polysulfide products. The polysulfide products are then discharged through an outlet **31a**, **31b** and, similarly, the recovery products can be discharged through outlet **40**, if desired. While discharge takes place all of the flags are rotated such that coupons **19a**, **19c**, **19e**, **19g** are positioned within the recovery zone vessel **92**, while coupons **19b**, **19d**, **19f**, **19h** are positioned within the first and second polysulfide zone vessels **90**, **94**. The recovery zone and polysulfide zone vessels are then refilled with their respective fluids, oxygen-containing gas flows through gas inlet **36**, and the recovery zone and polysulfide zone processes continue. While in this embodiment, the vessels can be filled and discharged simultaneously. Alternatively, the vessels may be filled or discharged in any other manner. In addition, the flags may be rotated at any one or more time periods between filling and discharging of the recovery and polysulfide generation zone vessels.

As discussed above, the efficiency of performing polysulfide generation and recovery can be increased by creating as many contact points as possible between the oxidation promoter element and the reaction fluids, e.g., by agitating the fluids. Preferably, this is accomplished in a continuous process whereby the white liquor and the sodium hydroxide solution flow through vessel 1 **21a** and vessel 2 **21b**. Consequently, one of more baffles may further be used in any of the vessels to increase the efficiency of the system. In the embodiment shown in **FIGS. 21** and **22**, the vessels **90**, **92**, **94** include baffles **50a-i** at spaced locations disposed along the length of the vessels. The baffles are suitably spaced to permit flags **47a-h** to rotate between two neighboring baffles. The baffles typically do not extend the full height or width of the vessel. The baffles, moreover, extend from the top, bottom and/or sides of the vessel, preferably the entire width of the vessel such that fluids flow over and/or under each baffle. However, it is noted that the baffles may be designed in any suitable manner to permit the reaction fluids to flow over, around, above, below and/or through the baffles so as to become agitated and increase the interaction between the oxidation promoter element and the reaction fluids.

The movement of fluid in one of the tank vessels is shown by dashed line **100** in **FIG. 21**. In particular, three baffles **50a-c** extend from a bottom wall of vessel **90** at spaced locations such that when flags **47a**, **47c** or flags **47b**, **47d** are rotated to permit their respective coupons to be situated in vessel **90**, the flags extend between two neighboring baffles or a baffle and a side wall of vessel **90**. Thus, the combination of

baffles and flags in vessel **90** creates a tortuous flow path for fluid flowing between inlet **30** and outlet **31**. As previously noted, baffles may be placed at any one or more suitable locations within each vessel to establish any desired flow path for fluid flowing within and the vessels and contacting the coupons disposed therein.

FIGS. 23 and 24 disclose a system configuration having a recovery zone and a polysulfide-generating zone that includes a rotary disc. Here, a tank **82** is provided with inlet **30** and outlet **31** ports. The oxidation promoter element, moreover, includes a disc substrate. The size and/or geometry of the disc substrate is not limited to any particular configuration. Preferably, a plurality of discs is provided having a diameter of about four meters and a thickness of about 0.6 centimeters. In addition, each disc substrate in the plurality may comprise identical or differing coating formulations placed thereon. In the embodiment illustrated in **FIG. 24**, the oxidation promoter element includes a plurality of disc substrates coated with a coating material having the oxidation promoter partially embedded therein (as described above). The oxidation promoter may be disposed at any selected locations within the coating and along the disc substrates. For example, the oxidation promoter may be disposed over substantially the entire surface area of the disc substrates or, alternatively, over selected portions of the disc substrates. The one or more oxidation promoter discs **60a-f** are connected to a rotary shaft **62**. Shaft **62** is driven by a conventional motor (not shown), and is suitably positioned to permit a portion of the disc to be contained within the tank and a portion of the disc to be exposed outside the tank. If more than one disc is present, the discs are spaced apart (e.g., 0.5 inches apart) to enable air and liquid flow between them. Situated above the discs and connected to the tank is a pressure controlled ventilation (PCV) chamber **86**. An oxygen-containing gas is supplied to the chamber via conduit **80**. Chamber **86** controls the flow of oxygen-containing gas over the exposed disc portions.

In use, the white liquor enters tank through inlet **30**, flowing through the tank and between discs **60a-f**. The discs are positioned such that a portion of each disk is immersed in the white liquor. The immersed portions contact the flowing white liquor, generating polysulfide products. The reacted, orange liquor continues to flow through tank **82**, and can be discharged through outlet **31**. After the desired reaction time expires, the discs can then be suitably rotated to expose the reduced portion of the disc (i.e., the portion that was immersed in the white liquor) to the oxygen-containing gas flow of the PCV chamber, as well as to immerse the recovered portion (i.e., the portion originally

exposed to the oxygen containing gas) in the white liquor. Alternatively, discs **60a-f** can be continuously rotated at the same or differing rates to facilitate the continuous performance of the polysulfide generation and recovery zones. The system of **FIGS. 23** and **24** is a continuous process, with liquor continuously flowing through the system and the oxidation promoter element being selectively positioned in either or both of the recovery and polysulfide generation zones during the process.

An exemplary embodiment utilizing the system of **FIGS. 23** and **24** is described below, in which about 33 liters per second of white liquor is continuously processed, utilizing MnO₂ as the oxidation promoter element, to form orange liquor containing about 5 grams per liter of polysulfide. Each disc in the system has a diameter of 4 meters and is situated within the system such that about half the surface area of the disc extends within the tank and the other half extends within the ventilation chamber (i.e., about half the surface area of each disc is exposed at any given time to white liquor flowing through the system). Each disc has a thickness of 0.635 centimeters, with a gap between neighboring discs also being 0.635 centimeters. The thickness of the coating on each disc substrate, including the oxidation promoter element, is 0.079 centimeters. The coating can be any of the previously described coatings (e.g., a formulation sold under the tradename Impreglon™ 817, available from Impreglon, Inc., Houston TX).

To produce polysulfide at the rate of about 5 grams/liter (measured as sulfur) in the orange liquor when processing white liquor at a flow rate of about 33 liters per second, where a retention time in which white liquor contacts the rotating discs is about 1 second, requires a total surface area of the discs, and thus the area of exposure to the oxidation promoter element, of from about 1,250 square meters to about 2,500 square meters. The total number of 4 meter diameter discs required to ensure a sufficient disc surface area for exposure to the white liquor is about 100 discs to about 199 discs. The discs are secured to a shaft to facilitate continuous rotation of the discs at a rate of about 10 revolutions per minute (RPM) to about 1000 RPM, preferably about 10 RPM to about 500 RPM, and most preferably about 150 RPM to about 500 RPM. A selected rotational rate of the discs ensures effective conversion of sodium sulfide to polysulfide by the oxidation promoter element portions of each disc that are submerged in the tank while simultaneously regenerating oxidation promoter element portions of each disc that are situated in the ventilation chamber.

EXAMPLES

A single-vessel configuration was used for the following examples in which polysulfide is generated in accordance with the present invention. The vessel for each experiment was either a 2-liter glass vessel or a 2.5-liter stainless steel vessel. Process conditions were controlled via a control panel.

The vessel was equipped with a heating jacket, a cooling coil, and a PID temperature controller to maintain the desired temperature. Temperature regulation is important because polysulfide production is dependent on temperature, and white liquor oxidation is an exothermic reaction. Lack of temperature regulation may result in producing thiosulphate.

For the oxidizing promoter element, the substrate was stainless steel and formed into coupons, approximately 1-inch x 9-inch with 1/8-inch thickness. The coating material was composed of polymeric formulations, including carbon, silicon, and iron, available from Impreglon, Inc., Houston, Texas. This coating material was sprayed on the substrate. The oxidation promoter, MnO_2 in powder form, was applied to each of the coated substrate coupons, where it became fixed to the coating material upon contact. The amount of MnO_2 needed for the experiment was determined based on the 1:1 molar ratio of MnO_2 to sodium sulfide proposed by Barker in U.S. patent No. 3,470,061, which is incorporated herein by reference in its entirety. The coupons were then baked in an oven, after which the finished MnO_2 -coated coupons were fixed to two stainless steel rings to form what is referred to as the “sleeve” configuration of the oxidizing promoter element (i.e., similar to the configuration described above and illustrated in **FIG. 11**).

For each experiment, the sleeve was inserted into the vessel such that it rested at the bottom of the vessel. The vessel was filled with 1 liter of clarified white liquor from Potlach or E. B. Eddy and then sealed and purged with nitrogen for 15 minutes to remove excess oxygen in the vessel above the white liquor surface. An outlet vent at the top of the vessel was open to allow the nitrogen and excess oxygen to escape. After the nitrogen purge, the outlet vent was closed and the nitrogen pressure was increased to 15 psig. The liquor was then heated to the desired set point, approximately 80°C. During this heating stage, the mixing speed was 500 rpm.

When the desired temperature set point was reached, a liquor sample was withdrawn from the reactor. This sample was coded as time (t) = 0 minutes since no

oxidation had yet taken place. The mixing speed was then increased to 1500 rpm, and oxygen was introduced into the reactor through an open tube immersed in the liquor. The oxygen flow rate was based on system pressure and monitored with a mass flow controller. The gas-liquid mixing was done using a Hollow Shaft of $\frac{3}{4}$ -inch diameter and 7-inch length having attached at the end a 6-blade Ruston impeller of $1\frac{3}{8}$ -inch diameter and $\frac{3}{4}$ -inch height, which was also hollow so that gas could flow through it. When oxygen surfaced above the white liquor in the headspace of the vessel, it entered the hollow shaft through an opening near the top of the vessel and exited at the end of the hollow shaft submerged in the white liquor.

For each experiment, a sufficient number of samples were collected to produce a concentration vs. time curve. To prevent sample degradation, the samples were “capped” with nitrogen and immediately quenched in an ice bath prior to analysis, as described below.

The presence of polysulfide species was determined by gravimetric analysis. This consists of acidifying the filtered liquor sample in order to precipitate the elemental sulfur, which is the excess sulphur of the polysulfide. Each sample tested for polysulfide was first diluted with water and acidified in the presence of EDTA. The resulting milky solution was then filtered under vacuum. Finally, the polysulfide precipitate was dried and weighed.

The results are as follows:

Experiment #1	
Time	Polysulfide Concentration
(min)	(g/L)
0	0.2
7	2.8
9	3.5
11	4.2
14	5.0
17	6.2
20	7.2
25	7.8
30	4.8

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Experiment #2	
Time	Polysulfide Concentration
(min)	(g/L)
0	0.8
6.5	1.9
12	2.7
17	3.4
20	4.4
23	5.1
26	6.0
29	6.8
32	7.8
36	6.7

Experiment #3	
Time	Polysulfide Concentration
(min)	(g/L)
12	2.6
16	4.6
20	5.6
24	6.6
27	7.3
30.5	8.3
33	7.7
36	6.4

Experiment #4	
Time	Polysulfide Concentration
(min)	(g/L)
0	0.410
6	1.670
12	3.010
16	3.950
23	5.830
26	7.030
29	7.630
32	7.670
36	5.610

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Experiment #5	
Time	Polysulfide Concentration
(min)	(g/L)
0	0.4
6	2.1
12	3.6
18	5.6
24	7.4
27	9.0
30	8.1
32	6.2
34	5.5
37	4.0

Experiment #6	
Time	Polysulfide Concentration
(min)	(g/L)
0	0.7
6	1.7
12	3.9
18	5.5
22	7.7
25	7.9
28	8.5
32	6.9
36	4.5

Having described preferred embodiments of systems and methods for generating polysulfide, variations and changes will be suggested to those skilled in the art in view of the teachings set forth herein. It is therefore to be understood that all such variations, modifications and changes are believed to fall within the scope of the present invention as defined by the appended claims.